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BUBLEWITZ ET AL-14 PCT

In re Application of: Alexander BUBLEWITZ ET AL

Application No.: 10/589,329

Filed: AUGUST 14, 2006

For: DENTAL MATERIAL BASED ON ALKOXYSILYL-FUNCTIONAL POLYETHERS CONTAINING A SALT OF A STRONG BASE AS CATALYST

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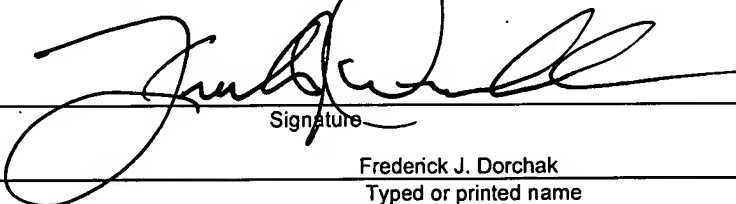
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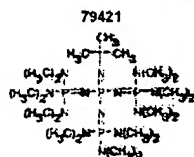
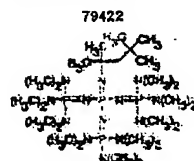
Strong and Hindered Bases in Organic Synthesis

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Introduction / Phosphazene Bases / Verkade's Superbases / Traditional bases
Preservation of Reagents / Aldrich Schlenk-Type Glassware / Miscellaneous Information**Phosphazene Bases**Introduction / Monomeric Phosphazene Bases (P1)
Dimeric Phosphazene Bases (P2) / Tetrameric Phosphazene Bases (P4)**Tetrameric Phosphazene Bases (P4)**The two P₄ phosphazene bases offered by Fluka differ slightly with respect to their steric hindrance and basicity (Table 5).Table 5. Order of Basicity for P₄ Bases

Order of steric hindrance:	P4-t-Oct	>>	P4-t-Bu
Fluka Product Number:	78422		79421
Basicity (^t MeCN pK _{BH+}):	42.7		41.9

P4-t-Bu^[1] 79421 and P4-t-Oct 78422, offered as 1 M solutions in hexane have several important features. They are highly sterically hindered, extremely hygroscopic, highly stable towards hydrolysis, 18 orders of magnitude more basic than DBU,^[2] and already in the basicity range typical of organolithium bases. Both 79421 and 78422 are particularly suitable for deprotonation (activation) of pronucleophiles, although also deprotonations for spectroscopic investigations,^[3-7] epimerisations,^[8] double bond shifts,^[9] β-eliminations,^[9-12] and Li⁺ complexation (alkyl-lithium activation)^[13,14] have been reported. See Table 6 for a list of our P₂ bases with their properties, package size etc.

Table 6. Phosphazene bases P₄Phosphazene base P₄-t-Bu solution1-tert-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2Λ⁵,4Λ⁵-catenadi(phosphazene)pure, ~1.0 M in n-hexane C₂₂H₅₃N₁₃P₄ Mr 633.7 [111324-04-0] 1 ml, 5 ml, 25 mlPhosphazene base P₄-t-Oct solution1-tert-Octyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2Λ⁵,4Λ⁵-catenadi(phosphazene)pure, 1.00 M ± 0.02 M in n-hexane C₂₆H₇₁N₁₃P₄ Mr 689.8 [153136-05-1] 1 ml, 5 ml

Applications: These bases attract increasing interest in the field of anionic copolymerisation^[13-18] and have also been utilized for solid-phase synthesis^[6] related to combinatorial chemistry.^[19,20] They have been reported to support alkylations,^[1,21-31] Michael-additions,^[15,32,33] aldol-reactions,^[28,34-37] epoxide-opening,^[17,19,38,39] acylations,^[40] sulfonylations,^[41] anionic oxy-Cope rearrangements,^[42] oxidation of carbanions^[37] and transition metal-induced coupling reactions.^[29,43] Among the successfully converted low acidic substrates are alcohols^[35,42], amides^[39,41], peptides (N- and C-activation),^[24] porphyrines,^[4] phosphines,^[26] H-phosphonates^[31], esters,^[5,25,27,35] β-alkoxyesters^[21] and -lactones^[23,2118], and β, γ, δ-lactones,^[23,30] triesters,^[40] sulfones,^[3,34] episulfones,^[28] benzothiazole,^[21] and benzyl aryl ethers,^[38] β-Hydroxy sulfones,^[34] phosphonothioates,^[31] enol triflates,^[40] benzofuranes,^[36] and subphthalocyanines^[44] are thus efficiently synthesized.

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